

Concentrations and compositions of polybrominated biphenyls, -dibenzo-p-dioxins and -dibenzofurans in technical polybrominated diphenyl ether preparations

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in textiles, electronic equipment and plastics.¹ The three major commercial products available in the market are penta-BDE, octa-BDE, and deca-BDE products. Due to their widespread use, persistence, and bioaccumulation potential, PBDEs are now ubiquitous environmental contaminants. In addition, PBDEs have been shown to be toxic. Like PBDEs, polybrominated biphenyls (PBBs) also had been used as flame retardants in the 1970s.^{2,3} In 1973, an accidental contamination of human food web with PBBs in Michigan revealed the toxicological threat of this group of chemicals. Combustion of the wastes containing PBDE and PBB materials may lead to formation of another class of highly toxic compounds such as polybrominated dibenzo-*p*-dioxins (PBDDs) and -dibenzofurans (PBDFs).^{4,5} Despite a continuous reduction in the worldwide annual production in the last decade, the occurrence of PBDEs, PBBs and PBDDs/DFs in the environment was recently confirmed in a wide range of samples.^{6,7} It is therefore important to evaluate potential sources of emission, especially PBBs and PBDDs/DFs, into the environment to estimate global inventories and to control emissions. To obtain this information, analysis of individual congeners in technical BDE preparations is needed. Technical BDE mixtures may contain PBBs and PBDDs/DFs as impurities. It is necessary to estimate release of PBBs and PBDDs/DFs from technical BDE usage. In this study, congener-specific analysis of bromodiphenyl ethers (BDEs) was carried out in technical BDE preparations. Technical BDE preparations were also analysed for PBBs and PBDDs/DFs to determine the magnitude of contamination using two-dimensional HPLC clean-up system with porous graphite carbon and pyrenyl ethyl columns, and HRGC/HRMS quantification.

Materials and methods

Technical preparations of PBDEs (DE-71, DE-79 (Lot numbers 1525DD11A and 8525DG01A), DE-83 and DE-83R (100% active ingredient)) were obtained from Great Lakes Chemical Corporation (West Lafayette, IN, USA). According to the manufacturers, the bromine contents of DE-71, DE-79, and DE-83 were 69%, 78%, and 82%, respectively. Technical BDE mixtures were dissolved in *n*-hexane (or toluene) and the diluted solutions were used for the quantification of individual BDE, PBB, and PBDD/DF congeners. Diluted PBDE standards were passed through a porous graphite carbon column (Hypercarb; 100 x 4.6 mm; 7 µm particle size) for fractionation (Figure 1). Details of the fractionation procedure have been described elsewhere.⁸ The first fraction, eluted with 50% dichloromethane (DCM) in *n*-hexane at a rate of 2.5 ml/min (15 ml), contained PBBs and most of the PBDEs. Hypercarb column was then reversed and eluted with toluene (45 ml) to collect PBDDs/DFs.

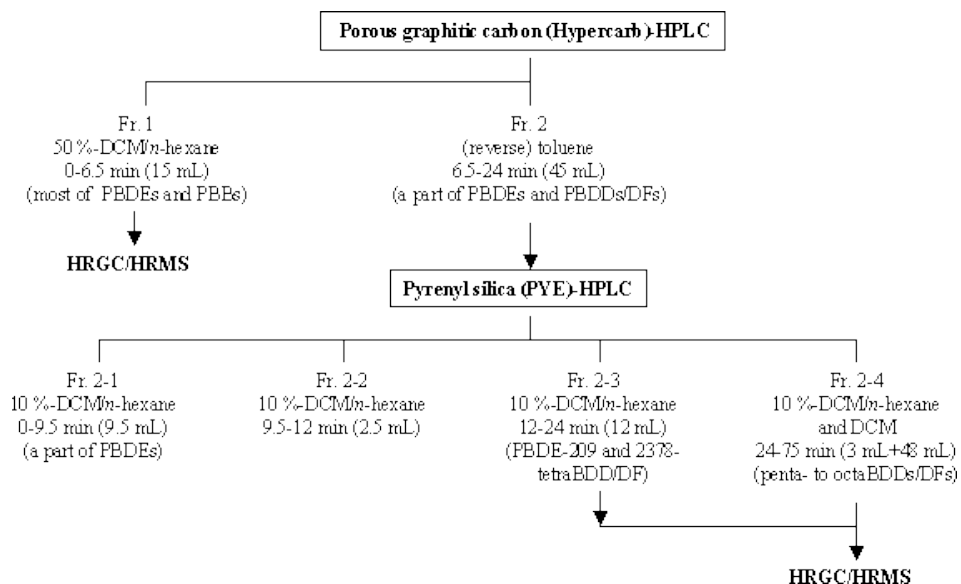


Figure 1. Analytical procedure for PBBs and PBDDs/DFs.

The toluene fraction was further fractionated by passing the extracts through a Cosmosil 5-PYE column (pyrenyl ethyl group; 250 x 4.6 mm, 5 μ m particle size). The first and second fractions, eluted with 12 ml of 10% DCM in *n*-hexane, contained highly brominated DE congeners. The third fraction, eluted with the same solvent mixture contained lower brominatedDDs/DFs and deca-BDE, IUPAC No. 209. The fourth fraction, eluted with 3 ml of 10% DCM in *n*-hexane and 48 ml DCM, contained the remaining PBDD and PBDF congeners. This fractionation enabled us to isolate PBDFs from PBDEs, which would otherwise coelute in a GC column. Each fraction was concentrated and injected into an HRGC interfaced with an HRMS. A Hewlett Packard 6890 Series II GC interfaced with a MicromassAutospec-Ultima HRMS was used for the determination of di- to octa-brominated biphenyls, tetra- to octa-brominateddibenzo-*p*-dioxins and -dibenzofurans. The mass spectrometer was operated in an electron impact (35 eV energy and 500 mA ion current), selected ion monitoring (SIM) mode at a resolution $R > 10,000$ (10% valley). Separation of PBDE, PBB and PBDD/DF congeners was achieved using a DB5 capillary column (0.25 mm i.d. x 15 m length; 0.10 μ m film thickness). The column oven temperature was programmed from 150 $^{\circ}$ C (1 min) to 300 $^{\circ}$ C at a rate of 5 $^{\circ}$ C/ min, with a final hold time of 10 min. The internal standards from Cambridge Isotope Laboratories (Andover, MA, USA) were used (EDF-5071 and EDF-5073; 13 C-labelled PBDDs/DFs) to check recovery ratio through the analytical procedure. Firemaster BP-6 (AccuStandard, New Haven, CT, USA) and EDF-5059 (CIL, Andover, MA; PBDD/DF mixture), were used to identify and quantify PBB and PBDD/DF congeners, respectively.

Results and discussion

High resolution gas chromatographic analysis of Firemaster BP-6 revealed the presence of 10 peaks in this study. Hexa-BB was the predominant homologue in Firemaster BP-6. The major BB congeners in Firemaster BP-6 were hexa-BB (IUPAC No. 153) and hepta-BB (No. 180). Brominated biphenyl composition in Firemaster BP-6 is similar to those of the results published earlier. Brominated biphenyls nos. 153 and 180 were quantified in three technical BDE preparations (DE-71, DE-79 - Lots 8525DG01A and 1525DD11A) investigated using the reference BB% quantification factor.⁹ Technical BDE preparations contained PBBs, as impurities, at several hundreds to thousands of nanogram per gram concentrations. Concentrations of total PBBs in DE-71, DE-79 (8525DG01A) and DE-79 (1525DD11A) were 490, 2360 and 4630 ng/g, respectively. Compositional profile of individual BB congeners (BB-153 and -180) found in technical DE preparations are shown in Figure 2. The ratios of BB-180 to total PBBs were 17, 37 and 70% in DE-71, DE-79 (8525DG01A) and DE-79 (1525DD11A), respectively. Concentration of total PBBs in technical preparations increased with an increase in BB-180 content, suggesting the dependency of ratio of highly brominated DE congeners in technical BDE preparations. Minor components of PBBs, that were detected in Firemaster BP-6 (which contained trace amounts, 70 ng/g, of these congeners) were not detected in technical DE preparations. The occurrence of PBBs at nanogram per gram levels in BDE preparations suggests the environmental emission of PBBs from the use of PBDEs. Earlier studies have reported the occurrence of polychlorinated naphthalenes (PCNs) and -dibenzofurans (PCDFs) at microgram per gram level in technical PCB preparations.¹⁰⁻¹²

Technical BDE preparations contained relatively lesser concentrations of PBBs as impurities relative to PCNs in PCB preparations.

We could identify and quantify 2,3,7,8-substituted bromodibenzo-*p*-dioxins and -dibenzofurans, such as 2,3,7,8-tetra-BDD/DF, 1,2,3,7,8-penta-BDD/DF, 2,3,4,7,8-penta-BDF, 1,2,3,4,7,8-hexa-BDD/DF, 1,2,3,6,7,8-, 1,2,3,7,8,9-hexa-BDD, 1,2,3,4,6,7,8-heptaBDF and OBDD using the quantification standard, EDF-5059, without co-elution problems, by two-dimensional HPLC clean-up system, which enabled the congener-specific separation of PBDFs from PBDEs. Technical BDE preparations did not contain PBDD/DF congeners at a detection limit of 70 ng/g in this study. Further investigation using high resolution mass spectrometry regarding impurities in technical DE preparations, is necessary to understand the behavior of BBs/BDDs/BDFs in the environment and emission inventories in the world.

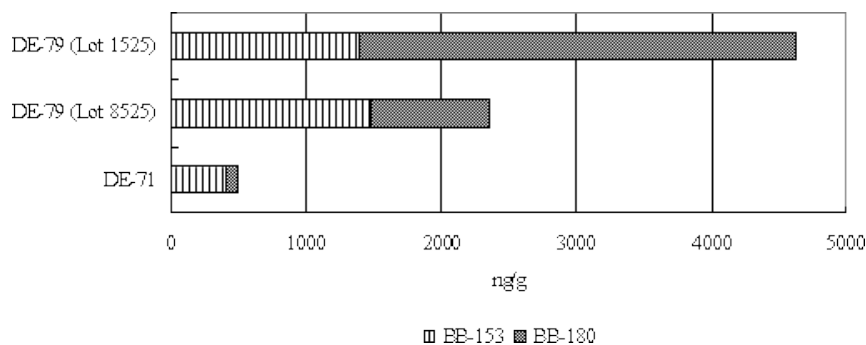


Figure 2 Compositional patterns of hexabromo biphenyl (BB-153) and heptabromo biphenyl (BB-180) congeners in technical bromodiphenyl ether (DE) preparations.

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